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LDRD PROJECT NUMBER: 179990

LDRD PROJECT TITLE: Microscopic Understanding of Fischer-Tropsch Synthesis on Ruthenium

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ABSTRACT: Total energy calculations and scanning tunneling microscope (STM) image simulations were conducted in an effort to interpret new experimental images of CO and H adsorbed on the close-packed surface of ruthenium metal. The images are remarkable in suggesting that the adsorbed species are intermixed, plausibly accounting for the superior catalytic activity of this metal in forming hydrocarbons. Insight was gained over the short duration of the project, but a more accurate method of simulating images will be required before contact between theory and experiment points to a final result.

INTRODUCTION: To make solar power viable at large scale, we need an economical way to store the captured energy, optimally in a liquid fuel. Sandia's Sunshine to Petrol Grand Challenge LDRD was aimed at a first step, developing cyclic reactors that use solar energy to generate syngas ($\text{CO} + \text{H}_2$) from CO_2 and H_2O . Much is known about the final step, the Fischer-Tropsch (F-T) process, combining carbon monoxide (CO) and hydrogen (H_2) over a catalyst to make liquid hydrocarbons. But new, atomic scale images of CO and hydrogen co-adsorbed on the most efficient of F-T catalyst materials, elemental ruthenium (Ru), promise deeper understanding of the catalytic pathway, and perhaps a more efficient F-T process. The new images remarkably suggest that adsorbed CO and hydrogen intermix on the ruthenium surface rather than segregating into pure CO and pure adsorbed hydrogen islands, as typically happens. Are they credible evidence for a mixed surface phase on ruthenium? If so, what is its nature? Does it help explain the superior catalytic F-T activity of ruthenium? The problem is that the STM images electron density, not atomic positions. Thus an interpretation based on first-principles computational modeling is needed. Density Functional Theory (DFT) calculations conducted for this purpose, produced binding energies vs. surface atom arrangement and simulated STM images, and might eventually address adsorbate vibration frequencies, and adsorbate-induced core-level shifts. The results generated should help to decipher the nature of key intermediates in F-T synthesis.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD: Total energies were computed, using the VASP DFT code, for numerous hypothetical mixed arrangements of adsorbed CO and H on the close-packed surface of ruthenium, with the goal of identifying low-energy arrangements. Using the Tersoff-Hamann approximation, STM images were simulated for several seemingly promising candidate structures for comparison to the data. Several approaches to evaluating the formation energies of the various arrangements were considered.

In the end the energy of the low-temperature, periodic arrangement of unmixed H + CO, also seen in high-resolution images, was adopted as a physically meaningful reference. Such is needed if one is to explain how annealing converts the low-temperature unmixed arrangement to a mixed one.

RESULTS: Several ideas were developed that point toward a successful interpretation of molecular-scale images of an intermixed structure of hydrogen (H) and carbon monoxide (CO) on the close-packed surface of ruthenium. One is that structures containing less hydrogen are energetically more favorable. A second is that the only way to explain the STM images is with a symmetry-breaking ad-molecule arrangement. Specifically, the H atom populations of every other triangle of CO molecules must be different. The third is that the Tersoff-Hamann approximation is inadequate to the task of simulating the observed images. It does not yield a dark spot where a H-atom lies. Contact has therefore been initiated with Jorge Cerdá (Madrid) who has implemented a more sophisticated computational approach to image simulation, based on electron scattering theory, and including the nature of the probe tip. A collaborative effort with him should resolve the problem of H atoms not corresponding to dark image spots, and thereby make it possible to explore H + CO structures by comparing simulated to experimental images, and not just by attempting to minimize system energy. This may be important if energy barriers prevent the system from finding its lowest-energy state.

DISCUSSION: Intermediate states in catalytic processes are notoriously difficult to isolate and identify. Progress made in the course of this (short) LDRD effort suggests that the goal of understanding the mixed H + CO structures seen in scanning probe images will be reached before long, and provide an important clue toward explaining why ruthenium is the best Fischer-Tropsch catalyst.

ANTICIPATED IMPACT: Such an explanation would provide insight into developing a cheaper substitute for very costly ruthenium metal, and thus help make “Sunshine to Petrol” an economically competitive source of sustainable fuel.

CONCLUSION: The importance of capturing solar energy in the form of liquid hydrocarbons, and the progress made during the brief period of this LDRD justify a more serious investment in the project.



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